* * * * * * * * * Welcome to STN International
NEWS 1 Web Page URLs for STN Seminar Schedule - N. America NEWS 2 Sep 17 IMSworld Pharmaceutical Company Directory name change to PHARMASEARCH
NEWS 3 Oct 09 Korean abstracts now included in Derwent World Patents Index
NEWS 4 Oct 09 Number of Derwent World Patents Index updates increased
The state of the s
det 22 Deine Getsim has been improved
NEWS 8 OCT 29 AAASD no longer available
NEWS 9 NOV 19 New Search Capabilities USDATEUL and HODRES
- ION IS TORCENTER (SM) - New FOXICOLOGY file por assistant
The state of the state of stat
NEWS 12 NOV 29 DWPI revisions to NTIS and US Provisional Numbers
THE DEC TO WPINDEX/WPIDS/WPIX New and Revised Manual Code & Code
Diriot Homorody Search
and the state of t
TOW AVAITABLE OF STA
- TICIUS IOI DPCI
———— TOTA HAS DEEH LEIDAGED and moving to
NEWS 24 Feb 01 DKILIT now produced by FIZ Karlsruhe and has a new update frequency
NEWS 26 Mar 08 Gene Names now available in Drock Eliminated Effective 3/31/02
MEMS 2/ Mar 22 TOXLIT no longer available
NEWS 28 Mar 22 TRCTHERMO no longer available
NEWS EXPRESS February 1 CURRENT WINDOWS VERSION IS V6.0d,
CORRENT MACINIUSH VERSION IS V6 02 (FNC) AND V6 07 ()
COMMUNIT DISCOVER KILLE IS DAMED OF DEDUTINESS
- The operating Hours Plus Help Deck Availability
The state of the s
NEWS WWW CAS World Wide Web Site (general information)
Enter Mayor 6 22

Enter NEWS followed by the item number or name to see news on that specific topic.

All use of STN is subject to the provisions of the STN Customer agreement. Please note that this agreement limits use to scientific research. Use for software development or design or implementation of commercial gateways or other similar uses is prohibited and may result in loss of user privileges and other penalties.

FILE 'HOME' ENTERED AT 11:28:34 ON 27 MAR 2002

COST IN U.S. DOLLARS

SINCE FILE TOTAL ENTRY SESSION 0.21 0.21

FULL ESTIMATED COST

FILE 'CA' ENTERED AT 11:28:48 ON 27 MAR 2002

USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT. PLEASE SEE "HELP USAGETERMS" FOR DETAILS.
COPYRIGHT (C) 2002 AMERICAN CHEMICAL SOCIETY (ACS)

Copyright of the articles to which records in this database refer is held by the publishers listed in the PUBLISHER (PB) field (available for records published or updated in Chemical Abstracts after December 26, 1996), unless otherwise indicated in the original publications. The CA Lexicon is the copyrighted intellectual property of the American Chemical Society and is provided to assist you in searching databases on STN. Any dissemination, distribution, copying, or storing of this information, without the prior written consent of CAS, is strictly prohibited.

FILE COVERS 1907 - 21 Mar 2002 VOL 136 ISS 13 FILE LAST UPDATED: 21 Mar 2002 (20020321/ED)

This file contains CAS Registry Numbers for easy and accurate substance identification.

CAS roles have been modified effective December 16, 2001. Please check your SDI profiles to see if they need to be revised. For information on CAS roles, enter $\underline{\text{HELP ROLES}}$ at an arrow prompt or use the CAS Roles thesaurus (/RL field) in this file.

The P indicator for Preparations was not generated for all of the CAS Registry Numbers that were added to the CAS files between 12/27/01 and 1/23/02. As of 1/23/02, the situation has been resolved. Searches and/or SDIs in the H/Z/CA/CAplus files incorporating CAS Registry Numbers with the P indicator executed between 12/27/01 and 1/23/02 may be incomplete. See the NEWS message on this topic for more information.

=> s (chromic or chromous or chromate) and fluoride

15974 CHROMIC

760 CHROMOUS

26095 CHROMATE

192425 FLUORIDE

L1 1199 (CHROMIC OR CHROMOUS OR CHROMATE) AND FLUORIDE

=> 1 and (ligand or ligands)

1 IS NOT A RECOGNIZED COMMAND

The previous command name entered was not recognized by the system. For a list of commands available to you in the current file, enter "HELP COMMANDS" at an arrow prompt (=>).

=> s l1 and (ligand or ligands)

209660 LIGAND

140421 LIGANDS

L2 16 L1 AND (LIGAND OR LIGANDS)

=> s 12 and replacement and kinetics

89081 REPLACEMENT

634136 KINETICS

L3 0 L2 AND REPLACEMENT AND KINETICS

=> logoff

ALL L# QUERIES AND ANSWER SETS ARE DELETED AT LOGOFF

LOGOFF? (Y)/N/HOLD:Y

COST IN U.S. DOLLARS SINCE FILE TOTAL ENTRY SESSION

FULL ESTIMATED COST ENTRY SESSION 13.92 14.13

STN INTERNATIONAL LOGOFF AT 11:31:00 ON 27 MAR 2002

```
Welcome to STN International
                  Web Page URLs for STN Seminar Schedule - N. America
 NEWS
                  IMSworld Pharmaceutical Company Directory name change
 NEWS
          Sep 17
                  to PHARMASEARCH
 NEWS
                  Korean abstracts now included in Derwent World Patents
          Oct 09
                  Index
                  Number of Derwent World Patents Index updates increased
 NEWS
          Oct 09
                 Calculated properties now in the REGISTRY/ZREGISTRY File
 NEWS
          Oct 15
       5
          Oct 22 Over 1 million reactions added to CASREACT
 NEWS
 NEWS
          Oct 22
                 DGENE GETSIM has been improved
 NEWS 8
         Oct 29 AAASD no longer available
 NEWS 9
         Nov 19 New Search Capabilities USPATFULL and USPAT2
 NEWS 10
                 TOXCENTER(SM) - new toxicology file now available on STN
         Nov 19
NEWS 11
         Nov 29
                 COPPERLIT now available on STN
NEWS 12
                 DWPI revisions to NTIS and US Provisional Numbers
         Nov 29
NEWS 13
         Nov 30
                 Files VETU and VETB to have open access
NEWS 14
                 WPINDEX/WPIDS/WPIX New and Revised Manual Codes for 2002
         Dec 10
         Dec 10
NEWS 15
                 DGENE BLAST Homology Search
NEWS 16 Dec 17
                 WELDASEARCH now available on STN
NEWS 17
        Dec 17 STANDARDS now available on STN
NEWS 18 Dec 17 New fields for DPCI
NEWS 19 Dec 19 CAS Roles modified
NEWS 20 Dec 19
                 1907-1946 data and page images added to CA and CAplus
         Jan 25 BLAST(R) searching in REGISTRY available in STN on the Web
NEWS 21
NEWS 22
         Jan 25
                 Searching with the P indicator for Preparations
NEWS 23
         Jan 29
                 FSTA has been reloaded and moves to weekly updates
        Feb 01 DKILIT now produced by FIZ Karlsruhe and has a new update
NEWS 24
                 frequency
NEWS 25
         Feb 19
                 Access via Tymnet and SprintNet Eliminated Effective 3/31/02
NEWS 26
         Mar 08
                 Gene Names now available in BIOSIS
NEWS 27
         Mar 22
                 TOXLIT no longer available
NEWS 28
                 TRCTHERMO no longer available
        Mar 22
NEWS EXPRESS
              February 1 CURRENT WINDOWS VERSION IS V6.0d,
              CURRENT MACINTOSH VERSION IS V6.0a(ENG) AND V6.0Ja(JP),
              AND CURRENT DISCOVER FILE IS DATED 05 FEBRUARY 2002
NEWS HOURS
              STN Operating Hours Plus Help Desk Availability
NEWS INTER
              General Internet Information
NEWS LOGIN
              Welcome Banner and News Items
             Direct Dial and Telecommunication Network Access to STN
NEWS PHONE
             CAS World Wide Web Site (general information)
NEWS WWW
```

Enter NEWS followed by the item number or name to see news on that specific topic.

All use of STN is subject to the provisions of the STN Customer agreement. Please note that this agreement limits use to scientific research. Use for software development or design or implementation of commercial gateways or other similar uses is prohibited and may result in loss of user privileges and other penalties.

FILE 'HOME' ENTERED AT 10:56:32 ON 27 MAR 2002

=> file ca

COST IN U.S. DOLLARS

SINCE FILE TOTAL ENTRY SESSION 0.21 0.21

FULL ESTIMATED COST

FILE 'CA' ENTERED AT 10:57:14 ON 27 MAR 2002

:

USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT. PLEASE SEE "HELP USAGETERMS" FOR DETAILS. COPYRIGHT (C) 2002 AMERICAN CHEMICAL SOCIETY (ACS)

Copyright of the articles to which records in this database refer is held by the publishers listed in the PUBLISHER (PB) field (available for records published or updated in Chemical Abstracts after December 26, 1996), unless otherwise indicated in the original publications. The CA Lexicon is the copyrighted intellectual property of the American Chemical Society and is provided to assist you in searching databases on STN. Any dissemination, distribution, copying, or storing of this information, without the prior written consent of CAS, is strictly prohibited.

FILE COVERS 1907 - 21 Mar 2002 VOL 136 ISS 13 FILE LAST UPDATED: 21 Mar 2002 (20020321/ED)

This file contains CAS Registry Numbers for easy and accurate substance identification.

CAS roles have been modified effective December 16, 2001. Please check your SDI profiles to see if they need to be revised. For information on CAS roles, enter HELP ROLES at an arrow prompt or use the CAS Roles thesaurus (/RL field) in this file.

The P indicator for Preparations was not generated for all of the CAS Registry Numbers that were added to the CAS files between 12/27/01 and 1/23/02. As of 1/23/02, the situation has been resolved. Searches and/or SDIs in the H/Z/CA/CAplus files incorporating CAS Registry Numbers with the P indicator executed between 12/27/01 and 1/23/02 may be incomplete. See the NEWS message on this topic for more information.

=> s (chromium(III) or cr(III) or chromous) and (zinc or zn) MISSING OPERATOR 'CHROMIUM(III' The search profile that was entered contains terms or nested terms that are not separated by a logical operator.

=> s (chromium adj (III) or cr adj (III) or chromous) and (zinc or zn) MISSING OPERATOR 'ADJ (III' The search profile that was entered contains terms or nested terms that are not separated by a logical operator.

=> s chromium(III)

١,

MISSING OPERATOR 'CHROMIUM(III'

The search profile that was entered contains terms or nested terms that are not separated by a logical operator.

=> s chromium w III

268963 CHROMIUM

315848 W

894865 III

L1O CHROMIUM W III

(CHROMIUM(W)W(W)III)

=> s chromium adj III

268963 CHROMIUM

192 ADJ

894865 III

L20 CHROMIUM ADJ III

(CHROMIUM (W) ADJ (W) III)

=> s cr adj III

343444 CR

192 ADJ

894865 III

```
L3
              0 CR ADJ III
                  (CR(W)ADJ(W)III)
 => s chromium or cr
         268963 CHROMIUM
         343444 CR
 L4
         454538 CHROMIUM OR CR
 => s 14 and (ligand or ligands)
         209660 LIGAND
         140421 LIGANDS
          10585 L4 AND (LIGAND OR LIGANDS)
 L5
 => s 15 and replacement and kinetics
          89081 REPLACEMENT
         634136 KINETICS.
 L6
             43 L5 AND REPLACEMENT AND KINETICS
 => s 16 and (chromic or chromous or chromate)
          15974 CHROMIC
            760 CHROMOUS
          26095 CHROMATE
              6 L6 AND (CHROMIC OR CHROMOUS OR CHROMATE)
=> d 17 1-6 all
     ANSWER 1 OF 6 CA COPYRIGHT 2002 ACS
AN
     112:105809 CA
ΤI
     Oxidation of arsine by sodium dichromate in the presence of halide ions
ΑU
     Dorfman, Ya. A.; Polimbetova, G. S.; Mansurov, B. A.; Doroshkevich, D. M.
CS
     Inst. Org. Katal. Elektrokhim., Alma-Ata, USSR
SO
     Zh. Obshch. Khim. (1989), 59(9), 2007-12
     CODEN: ZOKHA4; ISSN: 0044-460X
DT
     Journal
LΑ
     Russian
     67-2 (Catalysis, Reaction Kinetics, and Inorganic Reaction Mechanisms)
CC
     Section cross-reference(s): 65
     The kinetics and mechanism of AsH3 oxidn. by Na2Cr2O7 were studied at
     293 K in a flow reactor with the capacity for potentiometric measurements.
     The catalytic influence of H3O+, Cl-, Br-, and I- was established.
     Reaction capacities decrease in the order CrO3I- > CrO3Br- > CrO3Cl-.
     rate-limiting step is intramol. electron transfer in Cr(AsH3)O3X(H2O) (X
     = Cl, Br, I) intermediate complexes. The replacement of H2O at the X
     ligand site by halides increases the d. on Cr(VI) and retards the
     reaction. Effective charges on ligands in these complexes and their PH3
     analogs were calcd. by using a CNDO method.
ST
     oxidn arsine chromate halide catalyst; quantum study chromium 6
     complex; charge ligand chromium 6 complex
IT
     Oxidation catalysts
        (halide anions, for arsine by chromate)
IT
     Kinetics of oxidation
        (of arsine, by chromate, in presence of halide anions)
IT
     Electric charge
        (effective, on ligands in chromium(VI) arsine or
        phosphine complexes contg. halide ligands)
IT
     16887-00-6, Chloride, uses and miscellaneous
                                                    20461-54-5, Iodide, uses
    and miscellaneous
                       24959-67-9, Bromide, uses and miscellaneous
    RL: CAT (Catalyst use); USES (Uses)
        (catalysts, for oxidn. of arsine by sodium dichromate)
ΙT
    120045-52-5
                   120045-61-6
                                 120045-62-7
                                               120045-63-8
                                                             120065-24-9
    125565-77-7
    RL: RCT (Reactant)
```

```
(ligand effective charges in, quantum calcn. of, intramol.
          electron transfer in relation to)
       10588-01-9, Sodium chromate (Na2Cr2O7)
       RL: RCT (Reactant)
          (oxidn. by, of arsine in presence of halide anions)
 IT
       7784-42<u>-1</u>, Arsine
      RL: PRP (Properties)
          (oxidn. kinetics of, by sodium dichromate in presence of
         halide anions)
      ANSWER 2 OF 6 CA COPYRIGHT 2002 ACS
 AN
      90:61842 CA
      Mechanistic studies on the reactions of cis-diaquabismalonatochromate(III)
 TI
      ion with 2,2'-dipyridyl and 1,10-phenanthroline
 ΑU
      Chatterjee, C.; Basak, A. K.
      Dep. Chem., Indian Inst. Technol., Bombay, India
 CS
 so
      Indian J. Chem., Sect. A (1978), 16A(9), 758-61
      CODEN: IJCADU; ISSN: 0376-4710
 דת
      Journal
 LA
      English
 CC
      67-3 (Catalysis and Reaction Kinetics)
 AΒ
      Kinetic studies in aq. soln. on the replacement of the aqua ligands in
      cis-[Cr(Mal)2(OH2)2]- by 2,2'-dipyridy (dipy) and 1,10-phenanthroline
      (phen) forming [Cr(Mal)2(A-A)] - (A-A = dipy or phen) were made
      spectrophotometrically. Hitherto unknown mixed ligand complexes of
      Cr(III) in the form of K salts were also isolated and characterized. In
      both cases the anation reaction proceeds by a path purely 1st order with
      respect to the ligand concn. From the values of the rate consts. at 3 different temps. (at 50-70°), values of the activation parameters,
      \Delta H^* and \Delta S^*, are evaluated for each system. The values of the
      enthalpy of activation (\Delta H^*) for the present systems are fairly
     close to the corresponding values for the oxalato system suggesting a
     common mechanism involving outer sphere assocn. between the reacting
     complex and the entering ligand followed by transformation of the outer
     sphere complex into the product by an associative process. The results of
     the isokinetic plot (\Delta H^* vs. \Delta S^*) for the analogous Cr(III)
     systems are also indicative of the associative nature in the transition
     state for the present systems.
     deaquation malonato chromate; dipyridyl deaquation malonato chromate;
ST
     phenanthroline deaquation malonato chromate
IT
     Deaguation
       Kinetics of deaquation
         (of chromium malonato complex, by dipyridyl and
        phenanthroline)
IT
     66-71-7
                366-18-7
     RL: RCT (Reactant)
         (deaquation by, of chromium malonato complex,
        kinetics and mechanism of)
IT
     18485-09-1
     RL: RCT (Reactant)
        (deaquation of, by chelating agents, kinetics and mechanism
IT
     69030-48-4P
                    69030-49-5P
     RL: PREP (Preparation)
         (prepn. of)
L7
     ANSWER 3 OF 6 CA COPYRIGHT 2002 ACS
ΑN
     85:131201 CA
TI
     Rapid equilibration of the ethylenediamine-N,N,N',N'-
     tetraacetatoaquochromate(III) complex with chromate(VI), molybdate(VI),
     tungstate(VI), and azide. Labilization of the aquo ligand by the free
```

```
carboxylate and substitution at chromium(III)
 ΑU
      Sulfab, Yousif; Taylor, Roger S.; Sykes, A. Geoffrey
 CS
      Dep. Inorg. Struct. Chem., Univ. Leeds, Leeds, Engl.
 SO
      Inorg. Chem. (1976), 15(10), 2388-93
      CODEN: INOCAJ
 DT
      Journal
      English
 LΑ
 CC
      67-3 (Catalysis and Reaction Kinetics)
      Section cross-reference(s): 68
      Equilibration kinetic studies on the rapid complexation of
 AB
      ethylenediamine-N,N,N',N'-tetraacetatoaquachromate(III), Cr(edta)H2O-,
      with CrO42-, MoO42-, and WO42- were carried out by using the stopped-flow
      method at 25°, pH 7.3-8.7, and ionic strength 1.0 M (LiClO4).
      Replacement of the coordinated H2O, which is labilized by the free
      carboxylate arm of the edta, is obsd. Temp.-jump and stopped-flow studies
      of deaquation by N3- were also carried out at pH 4.3-5.4 and pH 7.38,
            The hydrogen ion dependence of the forward rate const., kf, is in
      all cases given by k1 + k2[H+], where k2 makes \leq25% contributions
      with MoO42- (VI) and N3- and \leq10% with CrO42- and WO42-. Rate
      consts. k1 (M-1 sec-1) are 3.2 \pm 0.2 (CrO42-), 21 \pm 2 (MoO42-), 27
      \pm 4 (WO42-), and 98 \pm 5 (N3-). Kinetic equil. consts. K1 = kf/kb
      are in good agreement with those obtained spectrophotometrically.
      equil chromium EDTA deaquation; EDTA chromium deaquation kinetics;
      chromate deaquation EDTA chromium; molybdate deaquation EDTA
      chromium; tungstate deaquation EDTA chromium; azide deaquation EDTA
      chromium
     Group VIB elements
     RL: USES (Uses)
         (deaquation by anionic forms of, of chromium EDTA complex,
        kinetics and equil. of)
IT
     Deaquation
       Kinetics of deaquation
         (of chromium EDTA complex, by azide and transition metal
        anions, reversible)
IT
     13907-45-4
                   14259-85-9
                                14311-52-5
                                             14343-69-2
     RL: RCT (Reactant)
         (deaquation by, of chromium EDTA complex, kinetics
        and equil. of)
IT
     19610-17-4
     RL: RCT (Reactant)
        (deaquation of, dianions, kinetics and equil. of)
     ANSWER 4 OF 6 CA COPYRIGHT 2002 ACS
L7
 Full Citing
Text References
AN
     79:58177 CA
     Mechanistic studies on the reactions of cis-diaquobis(oxalato)chromate(I
ΤI
     II) ion with 2,2'-dipyridyl and 1,10-phenanthroline
ΑU
     Banerjea, D.; Roy, J.
     Dep. Chem., Univ. Coll. Sci., Calcutta, India
CS
SO
     Z. Anorg. Allg. Chem. (1973), 399(1), 115-19
     CODEN: ZAACAB
DT
     Journal
LΑ
     English
CC
     67-3 (Catalysis and Reaction Kinetics)
     Section cross-reference(s): 22
     The kinetics of the replacement of the H2O ligands in
AB
     cis-Cr(H2O)2(C2O4)2- by 2,2'-dipyridyl (dipy) and 1,10-phenanthroline
     (phen) with formation of cis-Crdipy-(C2O4)2- and cis-Crphen(C2O4)2-,
     resp., was studied by spectrophotometry at 40-70°. The reaction
    followed 2 paths according to kobsd. = k0 + k1[L] (k = rate consts., L =
    dipy or phen). The const. k0 was identical for both systems [(3-10)
    \times 10-4 min-1], whereas k1 was slightly higher for phen than for dipy
    and k1/k0 was ~20. The activation parameters \Delta H_{\pm} were
```

₹

11.5, 19.8, and 20.8 kcal mole-1 and $\Delta S\pm$ were -46.7, -10.2, and -5.0 eu for k0, k1 (dipy), and k1 (phen), resp. The results suggest a dissocn. mechanism for the L-independent path (k0), where Cr-OH2 bond rupture is significant in the transition state, but significant bond formation by L in the transition state of the L-dependent path (k1). In the latter, simultaneous rupture of the two Cr-OH2 bonds in cis position is indicated by the $\Delta H\pm$ values.

ST deaquation chromium oxalato complex; dipyridyl deaquation chromium complex; phenanthroline deaquation chromium complex; kinetics deaquation chromium complex; mechanism deaquation chromium complex

IT Kinetics of deaquation

(of chromium oxalate complexes)

IT Deaquation

(of chromium oxalate complexes, mechanism of)

IT 66-71-7 366-18-7

RL: RCT (Reactant)

(deaquation by, of chromium oxalate complex, kinetics
and mechanism of)

IT 15489-30-2

RL: RCT (Reactant)

(deaquation of, by bipyridine and phenanthroline, kinetics and mechanism of)

L7 ANSWER 5 OF 6 CA COPYRIGHT 2002 ACS

Full Citing Text References

AN 68:99114 CA

TI **Kinetics** and mechanism of the reaction between the hexaaquochromic ion and the polyphosphate ion

AU Macarovici, Constantin G.; Stanisav, Costa; Niac, Gavril

CS Univ. Cluj, Cluj, Rom.

SO Rev. Roum. Chim. (1967), 12(6), 743-50 CODEN: RRCHAX

DT Journal

LA French

CC 67 (Catalysis and Reaction Kinetics)

Cr(NO3)3 soln. was poured progressively into the polyphosphate soln., AΒ until the ppt. formed just disappeared, this moment being termed t = 0. With progressive replacement of the ligand, the soln. color changed from violet to green; the color of the reaction product was similar to that of the [Cr(H2O)4Cl2]+. At diverse time intervals, 10 cc. samples were withdrawn, passed over a cationic exchange resin (Dowex 50 W, in H form, 50-100 mesh) column, the role of which is the retention of the $[\mathbf{Cr}(\mathrm{H2O})\,\mathrm{6}]$ +++ ions unengaged in the reaction with the polyphosphate, to allow study of the replacement of the 1st H2O mol. by an anionic group of the polyphosphate macromol. The concn. of the free Cr(III) ion at different moments was detd. by [Cr(H20)6]+++=f(t). Absorbance was detd. at λ = 370, 470, 530, and 680 m μ , and sometimes whole absorption spectra in the visible and uv were obtained. For tracing the [Cr(H2O)4Cl2]+ spectrum, CrCl3 was dissolved in H2O at 3°, and the spectrum was recorded at this temp. In order to detect the $[{\tt Cr}\,({\tt H2O})\,5{\tt Cl}]++$ at max. concn., the soln. was left for 1-2 hrs. at room temp. The soln. used for kinetic measurements was boiled for 15 min., to establish the final reaction product, which was pptd. by EtOH. After drying in air, the greenish tinted substance, contg. excess polyphosphate, with respect to Cr+++, was decompd. thermogravimetrically. Subtracting the large amt. of H2O, retained <400°, left 2 plateaus, one at 500° and one at 600-700°, corresponding to elimination of 2 H2O from the internal coordination sphere. The final product contained 4 H2O mols. which means that in this reaction, 2 H2O mols. can be replaced totally by anionic polyphosphate groups. The substitution of the last H2O mols. occurs only in the molten state, when a glass is formed, which is H2O sol. The resemblance between the spectra of the resulting polyphosphate and of the ion [Cr(H2O)4Cl2]+ confirmed that only 2 mols.

are substituted. In both cases the 16,000 cm.-1 band was cleaved into 3 bands, indicating an axial symmetry. The gradual disappearance of the initial ion [Cr(H2O)6]+++ and the appearance of the product ion-[Cr(H2O)4(-PO3-)2]+ could be followed spectrophotometrically, by the diminishing absorbance at 370 and 530 $m\mu$, and the increasing absorbance at 470 and 480 mµ. Examn. of the thermal gravimetric analysis curve demonstrated 2 stages in the reaction, with formation of [Cr(H2O)5(-PO3-)]++ in the 1st stage. The 2nd stage of the reaction was difficult to be analyzed kinetically, and hence, spectrophotometric data were collected for the 1st stage only, obtaining by calcn. the rate consts. at corresponding λ values: k370 = 3.4 x 10-5 sec.-1, and $k530 = 2.6 \times 10-5$. By means of the ion exchange resin, the influence of the 2nd stage was eliminated, obtaining values of 11.7 \times 10-5-15.5 \times 10-5 sec.-1 for the 1st stage. The slope of the plots of log [Cr(H2O)6]+++ vs. time indicated a 1st order reaction, with respect to this ion. The reaction is practically 0 order with respect to the polyphosphate ion, so that the total order of reaction was 1, indicating that substitution of the 1st H2O mol. by the (-PO3-) was of the SN1 type. Detns. at 40-55° allowed calcn. of the activation energy at E = 25,700 cal./mole, and of ΔS^* = 2 entropy units. The 2nd stage of the reaction progressed likely by the same order and by the same mechanism, which implies that the (-PO3-) group is fixed electrostatically in the external sphere or that a nucleophilic attack of SN1 I.P. (ion pair) type occurred, the presence of the (-PO3-) ligand influencing solely the rate const. without modifying the mechanism.

ST CHROMIC ION WATER RELEASE; PHOSPHATE WATER SUBSTITUTION; WATER PHOSPHATE SUBSTITUTION

IT Entropy

(of activation, of substitution reactions of hexaaquachromium(3+) with polyphosphates)

IT Activation energy of substitution reactions

Kinetics of substitution reactions

(of hexaaquachromium(3+), with polyphosphates)

IT Substitution reactions

(of hexaaquachromium(3+), with polyphosphates, mechanism of)

IT Polyphosphates

RL: RCT (Reactant)

(substitution reactions of, with hexaaquachromium(3+), kinetics and mechanism of)

IT 14873-01-9

RL: RCT (Reactant)

(substitution reactions of, with polyphosphates, **kinetics** and mechanism of)

L7 ANSWER 6 OF 6 CA COPYRIGHT 2002 ACS

Full Citang Text Peferences

AN 66:98897 CA

TI Substitution reactions of oxalato complex ions. VI. The **kinetics** of the anation reaction of cis-bis(oxalato)diaquochromium(III) ion with oxalate ion in aqueous solution

AU Kelm, Hartwig; Harris, Gordon McLeod

CS State Univ. of New York, Buffalo, N. Y., USA

SO Inorg. Chem. (1967), 6(4), 706-11 CODEN: INOCAJ

DT Journal

LA English

CC 67 (Catalysis and Reaction Kinetics)

AB cf. CA 57, 4294i. The complex ion cis-Cr(C2O4)2(H2O)2- undergoes reaction in aq. soln. with either HC2O4- or C2O42- ion to give the tris(oxalato)chromium(III) complex ion. The rate-detg. step appears to be ligand water dissocn. from the diaquo complex ion, following an outersphere associative equilibration of the latter with bioxalate or oxalate ion. The observed pseudo-first-order rate const. is described by

k = kw[K1(HC2O4-)/[1 + K1(HC2O4-)] + K2(C2O42-)/[1 + K2(C2O42-)]], whereK1 and K2 are the assocn. consts. for bioxalate and oxalate, resp., and kw is the rate const. of the water replacement. K1 and K2 have values of 0.85 and 1.9, resp., at 50° and are independent of the ionic strength, I. At 50°, kw varies between about 10-3 sec.-1 at I = 0 and about 7 \times 10-3 sec.-1 at I = 2.7M. The ionic strength effects are not altered by changes in the nature of the "inert" 1-1 electrolyte used. Temp. dependence studies indicate that the enthalpy of activation of the rate-detg. process is close to 22 kcal./mole. 24 references. Substitution reactions (of oxalate ions for water in cis-diaquabis(oxalato)chromate (1+), mechanism of) Activation energy of substitution reactions

IT Kinetics of substitution reactions (of oxalate ions for water in cis-diaquabis(oxalato)chromate (1-))IT

15489-30-2 RL: RCT (Reactant)

IT

IT

=>

(substitution of oxalate ions for water in, kinetics and mechanism of)

338-70-5, reactions 920-52-5, reactions RL: RCT (Reactant) (substitution of, for water in cis-diaquabis(oxalato)chromate (1-), kinetics and mechanism of)

8 of 8